Combined DFT and Semi-Continuum Modelling of Space Charge Regions in Li_3OCl Solid Electrolytes.

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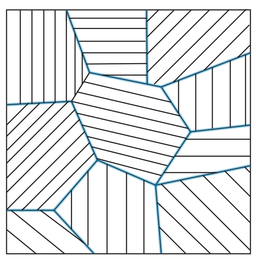
Context

Over recent decades lithium-ion batteries have become a dominant power source due to their high energy densities and low self-discharge rates, however there are safety concerns due to their use of flammable orgainc liquid electrolytes. Lithium rich anti-perovskites, such as Li_3OX, where X is a halide ion, are a promising family of solid electrolytes with the potential for improved safety in lithium-ion batteries.

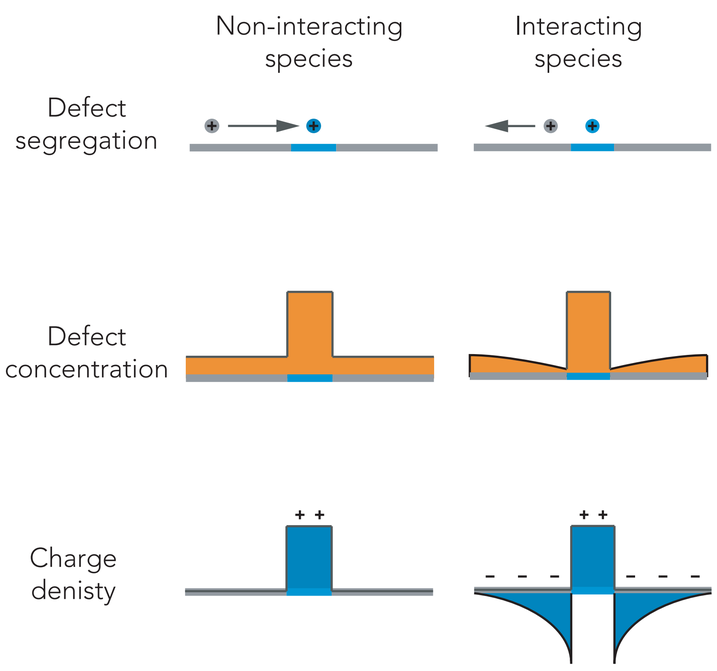
The presence of grain boundaries in Li_3OX strongly affects the transport of lithium ions, due to local changes in atomic structure and associated electrostatic potentials. These variations are key in the the formation of space charge regions and the respective affect on macroscopic ionic conductivities. In this work, we calculate space charge effects at three structurally different grain boundaries in Li_3OCl.

Grain boundaries and space charge formation

The structural distortion at grain boundaries affects the distribution of defects due to a variation in segregation energies and electrostatic energies, leading to the formation of space charge regions. This causes macroscopic ionic conductivities to differ compared to single crystals.

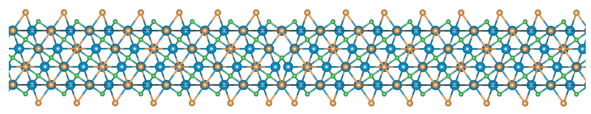


$$\sigma = nq\mu$$

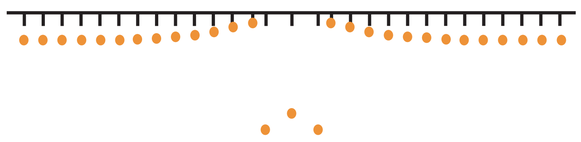


DFT and semi-continuum modelling of space charge formation

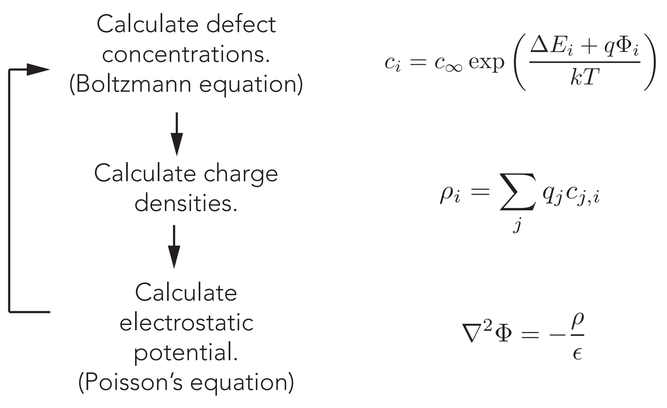
Grain boundaries are constructed using coincident site lattice theory and DFT is used to calculate the explicit defect segregation energies.



Defect segregation energies are mapped onto a 1D grid using atomic positions.



The 1D Poisson-Boltzmann equation is self-consistently solved using a finite difference approximation.



$$c_i = c_\infty \exp\left(\frac{\Delta E_i + q\Phi_i}{kT}\right)$$

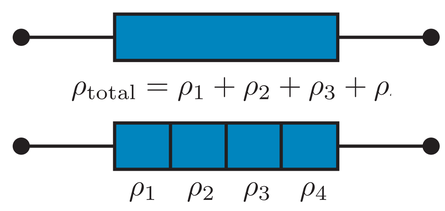
$$\rho_i = \sum_j q_j c_{j,i}$$

$$\nabla^2\Phi = -\frac{\rho}{\epsilon}$$

Calculating the resistivity ratio and activation energy

The grain boundary resistivity is calculated by taking each explicit site as a resistor in series. The resistivity ratio is the ratio of the total resistivity in the space charge region and the resistivity in the bulk.

$$\rho_{\text{total}} = \frac{1}{\sigma_{\text{total}}} = \frac{1}{c\mu z}$$



$$r_{GB} = \frac{\sum_i \rho_i}{\rho_\infty} = \frac{\sum_i \left(\frac{c_i z_i \mu_i'}{\Delta x_i}\right)}{\left(\frac{c_\infty z_i \mu_i'}{\Delta x_\infty}\right)}$$

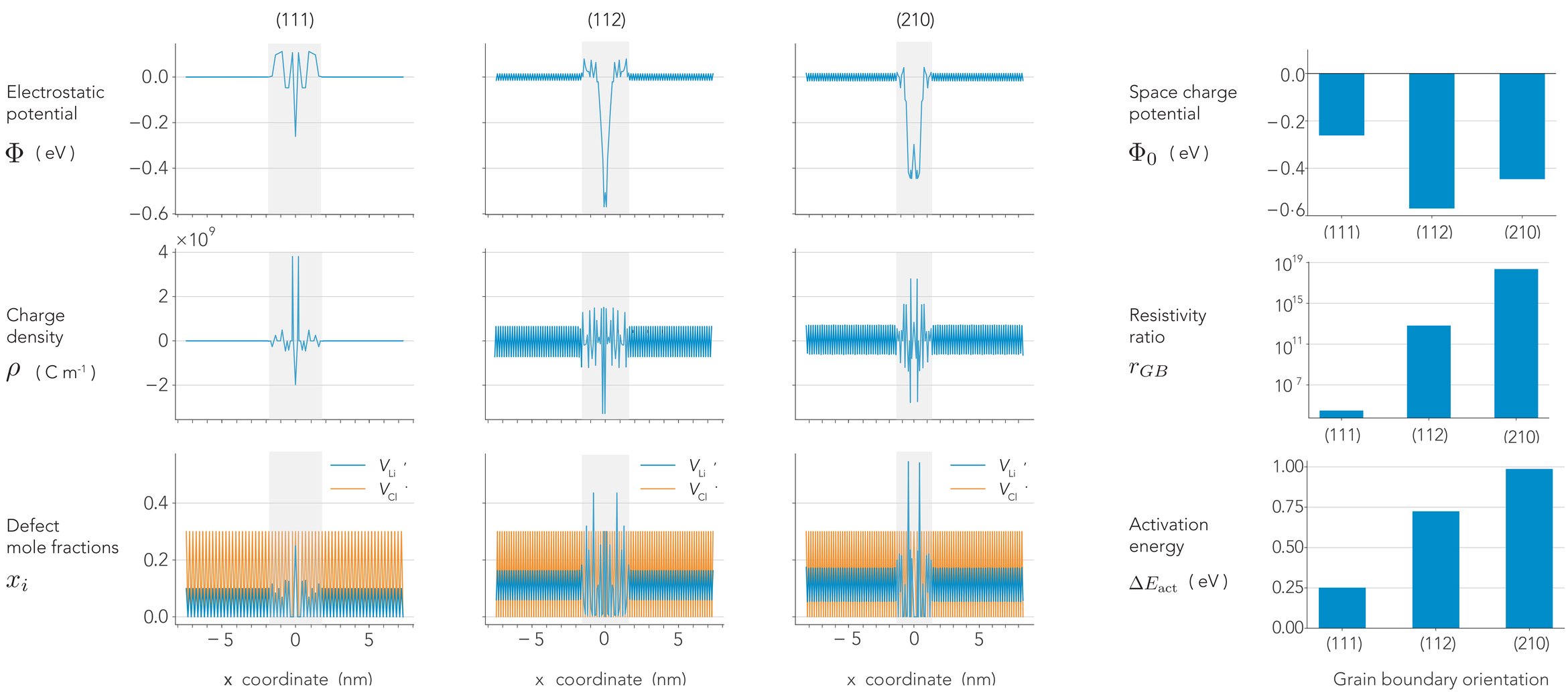
For particles on a lattice that only interact through volume exclusion, the mobility exhibits a "blocking term" changing the expression for the resistivity ratio.

$$r_{GB} = \frac{\sum_i \left(\frac{c_i z_i \mu_i'(1-x_i)}{\Delta x_i}\right)}{\left(\frac{c_\infty z_i \mu_i'(1-x_i)}{\Delta x_\infty}\right)}$$

The resistivity ratio can be calculated at a range of temperatures and numerical differentiation can be used to calculate grain boundary activation energies.

$$\Delta E_{\text{act}}^{\text{GB}} - \Delta E_{\text{act}}^{\text{bulk}} = -k\left(\frac{\delta \ln \rho}{\delta(1/T)}\right)$$

Calculated space charge properties



Conclusion

- A combined DFT and semi-continuum approach has been used to calculate the space charge properties of three structurally different Li_3OCl grain boundaries.
- In previous space charge models, the predicted resistivity ratio only depends on the the potential at the grain boundary core, ignoring the details of the defect distribution through the space charge region. Our approach takes into account the full defect distribution.
- The calculated space charge properties vary significantly with grain boundary orientation.

References

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